Study of Polymer–Polymer Interfaces: A Comparison of Ellipsometric and TEM Data of PMMA/PS and PMMA/SAN Systems

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ABSTRACT: Interfacial thickness data for a bilayer specimen of poly(methyl methacrylate) (PMMA) with polystyrene as well as poly(styrene-*ran*-acrylonitrile) containing 38.7 wt % acrylonitrile (SAN-38.7) obtained by ellipsometry and transmission electron microscopy (TEM) are compared, and good agreement is found. For TEM measurements an ultrathin section of the bilayer specimen was stained by RuO_4. A gray value distribution across the interface was obtained by image processing. The interfacial thickness measured by TEM for a PMMA/SAN-38.7 system annealed at 130 °C is 320 ± 30 Å, which is in excellent agreement with ellipsometric data reported previously. The interfacial thickness obtained by TEM for a PMMA/PS system annealed at 140 °C is 50 ± 30 Å, which is in fairly good agreement with a value of 30 Å measured by ellipsometry. The experimentally determined concentration profile of the PMMA/SAN-38.7 system is compared with different geometrical assumptions to fit the data such as linear gradient, hyperbolic tangent function (tanh), error function (erf), and squared sinusoidal function ($\sin^2$). The interfacial layer between PMMA and SAN-38.7 is asymmetric, and deviations from the geometrical assumptions have similar magnitudes, except the linear gradient, which leads to greater deviations and is not acceptable.

Introduction

Recently, ellipsometry has been used to obtain information on the interfacial thickness λ and the polymer–polymer interaction parameter χ_{AB} in immiscible polymer blends of either poly(styrene-*ran*-acrylonitrile) (SAN) or polystyrene (PS) with poly(methyl methacrylate) (PMMA).[1] Other authors also have studied the interfacial thickness of blends of PMMA and PS by using neutron reflection (NR) of a bilayer specimen[2,3] and of block copolymers.[3] Furthermore, it is possible to calculate the interfacial thickness from known χ_{AB} parameters by using appropriate theories.[4,5] This latter method has to be applied with caution because the χ_{AB} parameters given in the literature vary broadly and are dependent on the methods and conditions (such as temperature and concentration) used for the determination. From the relationship $\lambda \sim \chi_{AB}^{-1/2}$, one can see that small errors in χ_{AB} yield large errors in λ. Thus it has been found that the χ_{AB} values determined by small-angle neutron scattering (SANS) of miscible low-molecular-weight block copolymers of styrene and methyl methacrylate (assuming a random phase approximation)[6] are not in agreement with interfacial data obtained by NR.[3]

Experimentally determined interfaces between PS and PMMA range from 20 to 80 Å, depending on the sample's thermal history, the experimental temperature, the mathematical approximation of the concentration profile, and the method used. The most frequently reported value is about 50 Å. This value is close to the lower limit for accurate ellipsometric and transmission electron microscopy (TEM) measurements. Therefore, we replaced PS in PS/PMMA by SAN. Miscibility of SAN and PMMA depends on copolymer composition.[7-9] The observed miscibility window is found from approximately 9 to 34 wt % acrylonitrile in SAN. For a SAN copolymer just outside the miscibility window, a relatively thick interface is observed, because of the extremely small positive χ_{AB} parameter. In a previous article,[1] we used a SAN copolymer with 38.7 wt % acrylonitrile in SAN (hereafter called SAN-38.7) and observed a thick interface of 265–325 Å, measured by ellipsometry in the temperature range from 140 to 170 °C. This thick interface now enables us to obtain a nicely resolved concentration profile from TEM data. Because the relative error in ellipsometric measurements of the PMMA/SAN-38.7 system is also small, the ellipsometric values can be very well compared with TEM data. This correlation is especially important because ellipsometry cannot provide concentration profile data. To calculate interfacial thickness from data obtained by ellipsometry, a stepwise approximation must be used, assuming there is a uniform refractive index in the interfacial layer.[11] This approximation produces some uncertainties in the calculations, because an empirical correction factor to convert the step interface into a real interface has to be introduced.[21] Therefore, the correlation with TEM data, from which a concentration profile can be obtained, is welcome.

In order to compare the obtained values also a PMMA/PS system is studied by TEM. According to ellipsometric data this system should have an interfacial thickness of about 30 Å at 140 °C. Thus the TEM measurements should result in a narrower concentration profile in comparison with PMMA/SAN-38.7.

Experimental Section

All molecular weight data are listed in Table I. Bilayer specimens were prepared by mounting a thin film of SAN-38.7 (or PS) on top of a thick PMMA substrate.[11] The PMMA

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Table I
Molecular Weight Data for the Polymers

sample	source	M_w	M_w/M_n
PMMA	Sumitomo GI-633	151 000	2.1
PS	Denka-Styrol GP-1	180 000	2.0
SAN-38.7[a]	Mitsubishi Monsanto	74 000	2.2

[a] Number means wt % acrylonitrile in SAN.

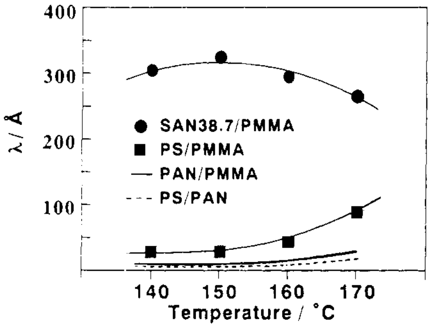

Figure 1. Interfacial thicknesses measured by ellipsometry for PMMA/SAN-38.7 and PMMA/PS systems. The interfacial thicknesses of PAN/PMMA and PAN/PS systems were calculated using eq 1 and data given in ref 1.

substrate was prepared between two silicon wafers in a hot press. Solutions (6 wt %) of SAN-38.7 in cyclohexanone and of PS in monochlorobenzene, respectively, were spin-cast on a silicon wafer, and the resulting films were floated off onto a water surface. The floating film was then picked up with the substrate. The bilayer specimens thus prepared were first dried in a vacuum oven for 24 h at 60 °C (hereafter called the "original sample"). The dried specimens were further annealed in a vacuum oven for a second 24-h period at 130 and 140 °C, respectively. It should be noted that the preparation of a bilayer specimen by direct spin-casting of a thin polymer layer on top of the substrate yields a thicker than normal interface as a result of the swelling of the substrate, even with very selective solvents. The ellipsometric measurements are described in detail elsewhere.[1]

The TEM measurements were done in a Zeiss EM 902 microscope with an acceleration voltage of 80 keV. The bilayer specimens were cut by an ultramicrotome, Ultracut S of Leica Co., in a direction normal to the film surface at room temperature. The ultrathin sections had a thickness of approximately 70 nm. They were stained with RuO_4 in the gas phase.[22] RuO_4 stained only the PS or the styrene in SAN and did not stain PMMA. The gray value distribution was obtained by using the image processing system (SEM/IPS) of Kontron Co. The line scans had a resolution of 512 points.

Results and Discussion

Figure 1 shows the interfacial thicknesses as measured by ellipsometry for PMMA/SAN-38.7 and PMMA/PS systems and the calculated interfacial thicknesses for PS/PAN (polyacrylonitrile) and PMMA/PAN systems in the temperature range from 140 to 170 °C. The interfacial thicknesses of PMMA/SAN-38.7 and PMMA/PS systems were measured directly by ellipsometry as a function of temperature.[1] The interfacial thicknesses between PAN and PS and between PAN and PMMA could not be measured directly because the interfaces were so thin that the error would be unacceptably large. However, in ref 1 the segmental interaction parameters $\chi_{S/AN}$ and $\chi_{AN/MMA}$ are reported for the temperature range under investigation. By using these parameters, it is possible to calculate the interfacial thickness λ which is then given by[5]

$$\lambda = \frac{2b}{(6\chi_{AB})^{1/2}}\left[1 + \frac{\ln 2}{\chi_{AB}}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)\right] \qquad (1)$$

where b is the Kuhn segment length (8 Å) and r_i is the number of segments.

As shown in Figure 1 all homopolymer pairs have very thin interfaces. Therefore, they are not very suitable for either TEM or ellipsometric measurements, even though the interaction parameter between PS and PMMA is generally considered to be very small. Thus the use of copolymers whose composition lies just outside the miscibility window seems to be a general method for generating thick and easily measurable interfaces. There is a dramatically increasing number of random copolymer blends showing a miscibility window[12] and it is easy to find suitable systems. For ellipsometric measurements, it is desirable that the components of the blend have a refractive index difference greater than 0.02. For TEM measurements, the two polymers must have different electron densities or selective staining properties. The system PMMA/SAN-38.7 fulfills both requirements. It has a refractive index difference of 0.064 at 130 °C (at a wavelength of 6328 Å), and SAN can be stained by RuO_4, which does not react with PMMA.

Figure 2a shows a TEM micrograph of an original sample, and Figure 2b shows the micrograph of an annealed sample. The white bottom layer represents the PMMA substrate and the dark layer is the stained SAN film. Both samples exhibit excellent flat surfaces and very uniform interfaces. Surprisingly, there is no significant difference between the two micrographs. Intuitively, one would think that the mechanical mounting procedure would create an imperfect interface and thermal annealing above T_g would change the interface. But the appearances of the interfaces in the original and the annealed specimens seem to be very similar. Also an ultrathin section of PMMA/PS was prepared in order to compare with PMMA/SAN-38.7 data (cf. Figure 2c). Again the PS film shows a relatively smooth surface. The PS film itself becomes partially structurated by RuO_4 staining; i.e. speckles are seen in the PS phase. The speckles seem to appear for highly stainable polymers, stained by RuO_4, and polybutadiene stained by OsO_4,[10] but there has not been any explanation for this behavior so far. From the visual inspection of Figure 2c one can already presume that the PMMA/PS interface is thinner than the PMMA/SAN-38.7 interface.

As an initial step in the comparison of the TEM and ellipsometric data we measured the thickness of the PS and SAN films. Because the interfacial thickness is calculated on the basis of a four-layer model, air/PS(SAN)/interfacial layer/PMMA,[11] a modified Drude equation was used for calculations.[13] Thus, from the characteristic parameters of ellipsometric measurements, the relative amplitude tan ψ, and the phase difference Δ,[14] the thickness of the PS (SAN) film and the interfacial thickness were simultaneously obtained by fitting them to the measured values of tan ψ and Δ. The thicknesses of the PS and SAN films measured by ellipsometry are about 0.5 and 0.35 μm, respectively, values that are in agreement with the TEM data.

To compare the interfacial thicknesses, concentration profiles over the interfacial layer were obtained by densitometric measurements of TEM images across the interface (Figure 3). The distribution of the gray values can be converted into a concentration profile.[15,16] As can be seen in Figure 3, there is a good resolution of the concentration profile, especially for the copolymer systems, by TEM measurements. This should mainly be caused by the small positive χ values of our copolymer system leading to a thick interface which can nicely be resolved by TEM measurements. Figure 4 shows the smoothed and normalized best fit curves. Normalized means that the gray value of the PMMA bulk phase was set to 0 and

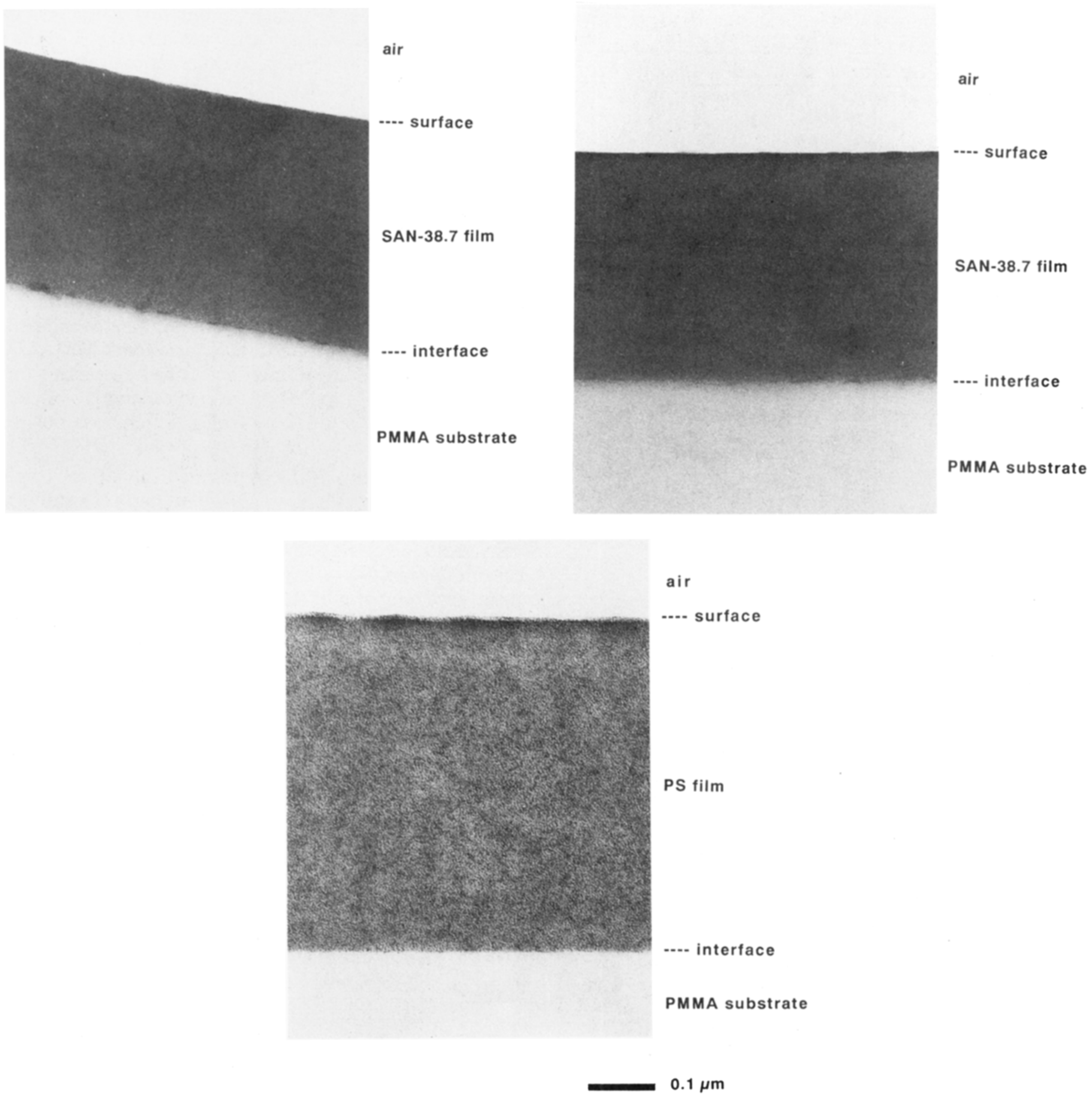

Figure 2. TEM photographs of ultrathin sections of the bilayer specimens stained by RuO_4: (a, top left) original PMMA/SAN-38.7 sample after drying at 60 °C for 24 h; (b, top right) PMMA/SAN-38.7 sample after additional annealing for 24 h at 130 °C, (c, bottom) PMMA/PS sample after annealing for 24 h at 140 °C.

the value of the SAN bulk phase was set to 1. The inset shows the definition of the interface used. The tangent was drawn at the inflection point creating a so-called wedge shape. The interfacial thickness λ is then defined as shown. Thus we obtained for both samples containing SAN-38.7 an interfacial thickness of about 320 Å. The error of the measurements is in the range ±30 Å. The value of 320 Å, valid for 130 °C, fits excellently with ellipsometric data shown in Figure 1. By using the same procedure the interfacial thickness in the system PMMA/PS is 50 ± 30 Å. This is in fairly good agreement with the value of 30 Å measured by ellipsometry at 140 °C. But it turns out that the copolymer system with a thick interface is more suitable to study by TEM and ellipsometry, because the relative error is very small for this system.

Furthermore, it should be interesting to compare different geometrical assumptions for the concentration profile across the interface with our experimental results. Figure 5 shows the experimentally determined concentration profile of the annealed PMMA/SAN-38.7 sample (solid line) in comparison with a number of geometrical assumptions. The calculations are fitted to an interfacial thickness of 320 Å, and the concentration of 0.5 is located at the center of the interfacial layer ($d = 0$, where d means distance). Firstly, it can be seen that the experimentally determined interface is asymmetric. This behavior was also observed in blends of PMMA and PVDF.[17] In the blend system under investigation the interfacial layer contains more SAN-38.7 than PMMA. This might be caused by a higher mobility of SAN-38.7 in comparison with PMMA. It can also be seen that the linear gradient, theoretically proposed by Brochard et al.,[18] does not result in a good fit. The linear fit would be of the form $\phi_{SAN} = (1/320)d + 0.5$. Better fits can be reached by using the squared sinusoidal function ($\sin^2$), frequently used for the description of concentration profiles in block copolymers,[19] the hyperbolic tangent function (tanh), proposed for polymer blends,[5] and the error function (erf), frequently

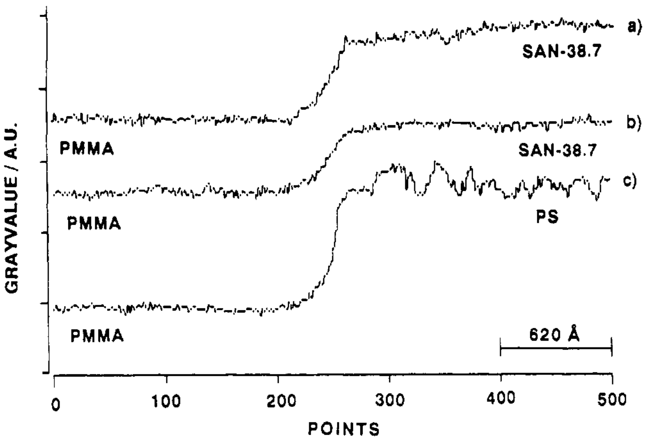

Figure 3. Densitograms of PMMA/SAN-38.7 and PMMA/PS bilayer specimens across the interface: (a) original PMMA/SAN-38.7 sample after drying at 60 °C for 24 h; (b) PMMA/SAN-38.7 sample after additional annealing for 24 h at 130 °C; (c) PMMA/PS sample after annealing for 24 h at 140 °C.

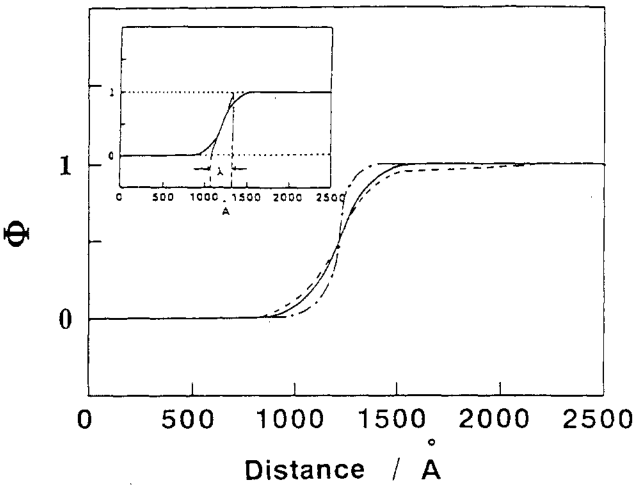

Figure 4. Normalized best fit curves of the concentration profiles of the original PMMA/SAN-38.7 specimen after drying for 24 h at 60 °C (- - -), of the same sample after annealing for 24 h at 130 °C (—), and of PMMA/PS (– · –) after annealing for 24 h at 140 °C. Φ is the concentration of SAN-38.7 and PS, respectively. The inset shows schematically the procedure to determine the interfacial thickness λ.

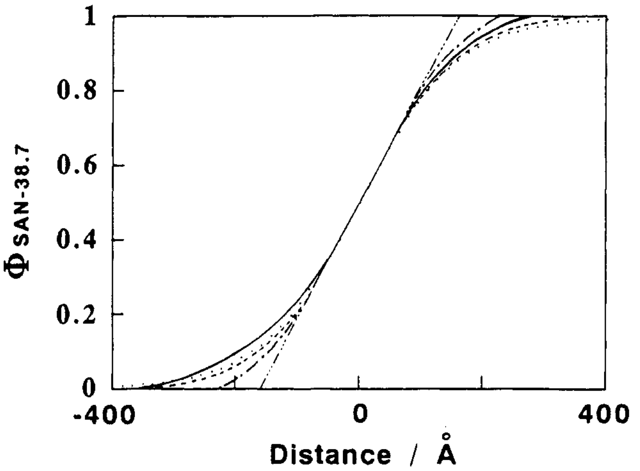

Figure 5. Concentration profiles across the interface. Experimentally determined profile for the annealed specimen of PMMA/SAN-38.7 (—), tanh (···), erf (- - -), sin² (– · –), and linear gradient (– ··· –).

used to describe diffusion profiles.[20] Equations 2–4 were used to obtain the concentration profiles in Figure 5. Recently, it has been found that the tanh gives the best fit.[3,15] But the approach to these results was different. In these cases the values where ϕ_{SAN} approaches to 0 and 1 were fixed. Thus the distance of 0 means not necessarily

$$\phi_{SAN} = \sin^2\left(\frac{d}{320} + \frac{\pi}{4}\right) \tag{2}$$

$(-80\pi \le d \le 80\pi,\ \phi_{SAN} = 0 \text{ at } d < -80\pi$ and

$\phi_{SAN} = 1 \text{ at } d > 80\pi)$

$$\phi_{SAN} = \frac{1}{2}\left(1 + \tanh\frac{d}{160}\right) \tag{3}$$

$$\phi_{SAN} = \frac{1}{2}\left(1 + \operatorname{erf}\frac{\sqrt{\pi}d}{320}\right) \tag{4}$$

a value for ϕ_{SAN} of 0.5. With this assumption the tanh function leads also in our case to a best fit. But, as can be seen in Figure 5, fixing $d = 0$ at $\phi_{SAN} = 0.5$ makes it impossible to distinguish which function fits the experimental data best. The deviations are mainly caused by the asymmetric behavior of the experimental values. A better fit could be obtained, e.g., for the tanh function by taking into account compressibility effects.[4]

Conclusion

Measurements of the interfacial thickness on bilayer specimens of PS/PMMA and SAN/PMMA by ellipsometry and TEM showed good agreement. It is important to confirm the ellipsometric data by an independent method because the computation of the interfacial thickness from ellipsometric data uses a number of constants (e.g. segment length, number of segments, refractive index of the interfacial layer) and correction factors which are connected with the concentration profile along the interface and not always well defined in a physical sense. The reliability of ellipsometry has been confirmed here, suggesting that ellipsometry is a powerful and convenient tool for the study of polymer/polymer interfaces.

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